

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(a): Hiroaki ABEKAWA

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Examiner: Charanjit S. Aulakh

For:

Method For Producing Propylene Oxide

DECLARATION OF Hiroaki ABEKAWA UNDER 37 C.F.R. 1.132

Honorable Commissioner of

Patents and Trademarks

Washington, D.C.20231

Sir:

I, Hiroaki ABEKAWA, a citizen of Japan, residing at 9-6-5-2306 Honmachi, Toyonaka-shi, Osaka, Japan declare that:

I graduated from Tokyo Institute of Technology, Department of Organic and Polymeric Materials, in March 1992.

I started to work for Sumitomo Chemical Company, Limited and have been studying catalysts for organic or inorganic synthesis since April 1992.

I have been studying zeolite catalysts since 1999 up to now.

I am the inventor of the above-identified application and am familiar with the subject matter thereof.

I have read the Office Action mailed with references cited therein and am familiar with the subject matter thereof.

I have made the following experiments in order to show that the presently claimed process has an unexpected superior results over the cited art.

## Experiments

### Experiment I.

Propylene oxidation reactions using the catalyst having an MWW structure containing Ti, the Ti having been incorporated during crystallization.

A reaction was carried out using a Ti-MWW catalyst having a Ti content of 1.1% by weight as determined by ICP emission spectrometry, prepared according to the method described in Chemistry Letters 774, (2000). A solution ( $H_2O_2$ : 5% by weight, water: 47.5% by weight, and acetonitrile: 47.5% by weight) was prepared using an 60% aqueous  $H_2O_2$  solution (product of Mitsubishi Gas Chemical), acetonitrile, and purified water. Twelve-grams of the solution thus prepared and 0.010 g of milled Ti-MWW catalyst was loaded into a 50 ml stainless steel autoclave. Then, the autoclave was transferred onto an ice bath and thereinto was loaded 10 g of liquid propylene. Further, it was pressurized to 2 MPa-G with nitrogen. The reaction was deemed started when 5 minutes passed after the autoclave had been placed in hot water bath maintained at 40°C when the inside temperature reaching about 35°C. One hour after the reaction starting, the autoclave was taken out of the hot water bath and sampling was conducted. The pressure at sampling starting was 3 MPa-G. The analysis was carried out by gas chromatography. As a result, the propylene oxide producing activity per unit catalyst weight was  $0.463 \text{ mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ . The propylene oxide selectivity based on propylene was 99.9%.

### Experiment II.

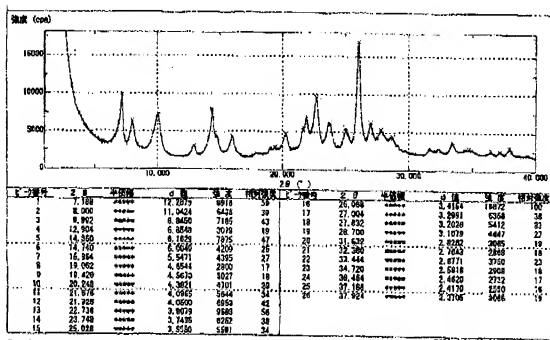
Comparative Experiment: Propylene oxidation reactions using Ti-de-Al-MCM-22 as catalyst according to USP 6,114,551.

#### 1) Preparation of Al-MCM-22

Al-MCM-22 (described in U.S. Pat. No. 4,954,325) recited at line 48, col.2 of U.S. Pat. No. 6,114,551 was prepared, and X-ray diffraction analysis of the obtained crystalline titanosilicate shown in Fig. 1 below has characteristic d-spacing maxima at 12.4

$\pm 0.25$ ,  $6.9 \pm 0.15$ ,  $3.57 \pm 0.07$ ,  $3.42 \pm 0.07 \text{ \AA}$  as disclosed at lines 25 to 36, col. 2 of U.S. Pat. 6,114,551.

2 $\theta$ /° lattice spacing d/Å  
 7.19 12.29  
 12.9 6.85  
 25.03 3.55  
 26.07 3.42



Peak No. d value Intensity Relative Intensity

Fig 1. XRD pattern of Al-MCM-22

## 2) Preparation of Ti-de-Al-MCM-22

1.0 g of Al-MCM-22 as prepared above was charged in a fused quartz tube, and subjected to dealumination with silicon tetrachloride at 500°C for 4.5 hours. The dealumination reaction was conducted by using a fused quartz tube and by continuously supplying silicon tetrachloride vapor mixed with nitrogen gas since it was described in U.S. Pat. No. 6,114,551 that removal of byproducts such as AlCl<sub>3</sub> was necessary.

Then, the supply of silicon tetrachloride was stopped and the

reaction tube was cooled to 450°C while substituting silicon tetrachloride with nitrogen. Thereafter, the nitrogen gas supply was stopped and dried by maintaining at 450°C for 1 hour under reduced pressure using a vacuum pump. Nitrogen gas was then supplied, and the pressure was returned to atmospheric pressure followed by cooling to 100°C.

Then titan was impregnated by continuously flowing titanium tetrachloride vapor mixed with nitrogen at 100°C for 24 hours. After stopping the supply of titanium tetrachloride, the reaction tube was cooled to room temperature under a flowing of nitrogen in place of titanium tetrachloride.

A mixture of nitrogen and water vapor, which was formed by bubbling nitrogen into water, was contacted with the resulting catalyst. Then the catalyst was dried at 125°C for 2 hours to produce de-Al-Ti-MWW(de-Al-Ti-MCM-22).

3) Oxidation of Propylene with Ti-de-Al-MCM-22 according to USP 6,114,551.

The obtained de-Al-Ti-MWW as above was used in the propylene oxidation reaction as in the Experiment I above. A solution containing 5 wt% H<sub>2</sub>O, 47.5 wt% water, and 47.5 wt% acetonitrile was prepared from aqueous 30% H<sub>2</sub>O<sub>2</sub> solution (product of Wako Pure Chemical Co.), acetonitrile and deionized water. 12 g of thus prepared solution and 0.010 g of crushed de-Al-Ti-MWW catalyst were charged in a 50 ml stainless steel autoclave. The autoclave was moved onto an ice-bath and 10 g of liquidated propylene were charged into the autoclave. The pressure in the reactor was raised to 2 Mpa (G) with nitrogen, and then the autoclave was put in a water bath kept at 40°C. The reaction was deemed started when 5 minutes passed after the autoclave had been placed in hot water bath maintained at 40°C when the inside temperature reaching about 35°C. After 1 hour, the autoclave was removed from the water bath, and a sample was withdrawn and analyzed by GC. The analysis revealed that the propylene oxide producing activity per unit catalyst weight was 0.00045 mol·h<sup>-1</sup>·g<sup>-1</sup>. The propylene oxide selectivity based on propylene was 5.1 %.

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Selectivity of propylene glycol, which is a consecutive reaction product of propylene oxide, was 94.9 %.

## Experimental Results

Table 1

Run	Catalyst	Catalyst Activity <sup>w1</sup> mol PO · h <sup>-1</sup> · g <sup>-1</sup> · catalyst	PO Select(%) <sup>w2</sup>
Exp. I	Ti-MWW	0.463	99.9
Exp. II	Ti-De-Al-MCM-22	0.00045	5.1

\* 1 : Propylene oxide producing activity per unit catalyst weight

## ※2 : Selectivity of Propylene Oxide based on Propylene

## Conclusion

As can be seen from the experimental results, the presently claimed method provided propylene oxide far better activity and selectivity as compared with the disclosed process of Levin et. al.

The presently claimed method is unexpectedly superior to the method of Levin et al.

I declare further that all the statements made herein of my own knowledge are true and that all statements made on information and belief are to be true; and further that those statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issued thereon.

**This**

28+L

day of April 2006

Hiroaki Abekawa

Hiroaki ABEKAWA